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PHASE- AND STRUCTURE-FORMATION PROCESSES DURING SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS IN THE SYSTEM $Al – MgCO_3 – SiO_2 – C$

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Phase and structure formation processes occurring in the system $Al – MgCO_3 – SiO_2$ in the course of self-propagating high-temperature synthesis are examined. The dependences of the structure and the phase composition of the composite materials formed on the ratio of the initial components are determined. It is shown that self-propagating high-temperature synthesis can be used to produce ceramic composite materials based on the spinel and silicon carbide phases.

Key words: self-propagating high-temperature synthesis, composite material, silicon carbide, spinel, phase formation, structure formation.

An effective method of obtaining composite materials is self-propagating high-temperature synthesis (SHS). SHS technology is a powder technology but it differs fundamentally from other powder technologies used in metallurgy by the fact that to realize synthesis powders are combusted and not heated in high-temperature facilities. The synthesis process proceeds by means of its own release of heat as a result of the interaction between the components of the initial mixture with valuable condensed products being formed, which makes it possible to decrease costs and reduce the energy consumption for production and, therefore, decrease prime costs [1]. Phase formation in the process of combustion of powdered mixtures occurs directly in the reaction volume, and the crystalline compounds formed grow into particles of other compounds. In the process it becomes possible to obtain composite crystalline phases, which is difficult to do under ordinary conditions. An example is a composition consisting of spinel and silicon carbide.

Aluminomagnesia spinel $MgO \cdot Al_2O_3$ is a ceramic material with adequate mechanical strength and good corrosion and radiation resistance; it is widely used in metallurgy, machine building, instrument building, the chemical industry as linings for inductors and electric resistance furnaces, filters for melts, high-temperature electric insulators, and articles for other purposes. Spinel ceramic finds wide applications in the manufacture of protective cases for thermocouples and crucibles for melting metals. Aluminomagnesia spinel is also a promising refractory material, used in heating equipment in its own form and with the addition of magnesia refractories during fabrication [2, 3].

The kinetic difficulties in the synthesis of spinel via the reaction

$$MgO + Al_2O_3 = MgAl_2O_4$$

make it necessary to perform the process at high temperatures [4, 5].

It is possible to produce spinel, while lowering energy consumption, from abundant raw materials by means of SHS in mixtures which include a magnesium-containing component and metallic aluminum [6, 7].

Together with spinel, silicon carbide based materials are a promising group. Since it is difficult to produce a strong, formed, article from pure silicon carbide, refractory articles with a high content of carbide are produced using various binders. Silicon carbide refractory materials and articles based on them possess a comparatively high electric and thermal conductivity, heat resistance, and durability under abrasion. They are not wetted by metal melts, possess high mechanical strength in the cold and heated states, and are slag-resistant. These properties make them promising for the production of different composite materials for metallurgy, including by the SHS method.

The synthesis of silicon carbide by SHS from mixtures containing silicon and carbon powder has been studied in a number of works, but because of the low exothermicity of

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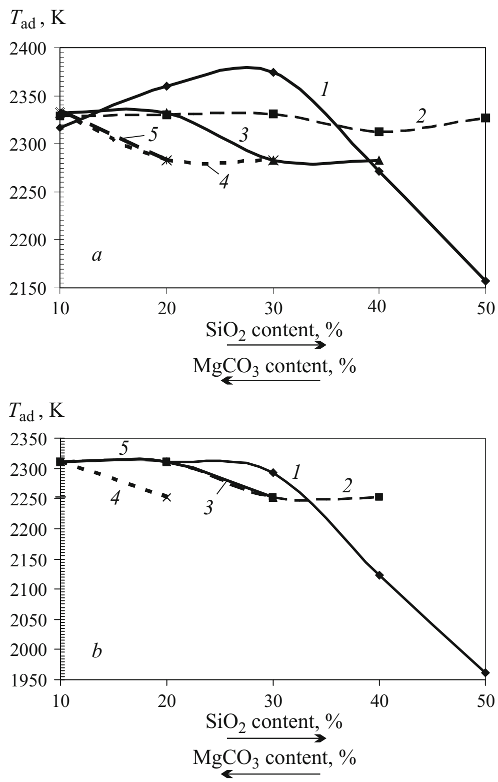

Fig. 1. Adiabatic combustion temperature versus the mixture composition with carbon content 10 wt.% (*a*) and 20 wt.% (*b*). Aluminum content (wt.%): *1*) 20; *2*) 30; *3*) 40; *4*) 50; *5*) 60.

the reaction the synthesis process was conducted with microwave irradiation or by passing an electric current [8, 9]. When SHS is conducted in mixtures of silicon and carbon oxides and metallic aluminum it is found that silicon-carbide refractory materials form in a composition with high-melting corundum and mullite phases [10, 11].

The production of spinel – silicon-carbide refractory materials and articles based on them is promising because these materials have high performance properties. This direction has been comparatively little studied, and the theoretical and technological aspects of the formation of the materials and the conduct of SHS require additional study in order to obtain compositions based on spinel and silicon carbide more efficiently.

We have investigated the mechanism of structure and phase formation during SHS of composite ceramic materials based on the phases $MgAl_2O_4$ and SiC in the system Al – $MgCO_3$ – SiO_2 – C.

Powdered magnesium carbonate, silica, aluminum powder, and carbon were used as the initial materials. Preweighed components were mixed and passed through a sieve. Samples in the form of cylinders or plates were prepared by semi-dry pressing with a PVC solution as the binder. The pressed samples were dried in a desiccator at 100°C to complete removal of moisture. To initiate SHS the dried samples were placed in a furnace heated to 800 – 900°C. The products of synthesis were studied by x-ray phase, electron-microscopic, and elemental methods of analysis. The electron-microscopic and chemical analyses were performed with a JSM-5610 LV scanning electron microscope with an EDX JED-2201 JEOL chemical-analysis system. A DRON-3 diffractometer was used for x-ray phase analysis; the JCPDS card file was used to interpret the diffraction patterns.

A thermodynamic calculation performed using the ASTRA-4 system of computer programs showed that the adiabatic combustion temperatures of the compositions in this system exceed 1950 K (Fig. 1). Evidently, the combustion temperature decreases as the silica and aluminum contents in the mixture increase. Under real conditions with 20%[3] aluminum content the reaction proceeds much less intensively; this is because the reduction process is impeded when the amount of the reducing agent present is too low. As the carbon concentration in the mixture increases, the combustion temperature of the compositions is observed to decrease because heat is expended to heat the carbon; under real conditions of synthesis carbon oxides formed during the oxidation of carbon by the oxygen in air carry away the heat.

Phase formation during combustion in the present system can be represented by the following basic processes:

$$MgCO_3 = MgO + CO_2; \quad (1)$$

$$4Al + 3CO_2 = 2Al_2O_3 + 3C \text{ (or CO)}; \quad (2)$$

$$MgO + Al_2O_3 = MgAl_2O_4; \quad (3)$$

$$3SiO_2 + 4Al = 3Si + 2Al_2O_3; \quad (4)$$

$$Si + C = SiC. \quad (5)$$

One would expect on the basis of the synthesis reactions (1) – (5) that silicon carbide would form without additional carbon being introduced into the mixture, since it is synthesized in the process of reduction of carbon dioxide. However, this is not observed, since incomplete reduction of carbon dioxide by aluminum probably predominates as the synthesis process proceeds and carbon monoxide is formed. In addition, the latter can be oxidized by the oxygen in air or diffuses out of the outer layers. In the absence of carbon in the system, the spinel diffraction peaks are likewise observed to become weaker, which is due to the decrease of the synthesis reaction temperature, and in consequence the interaction becomes weaker because of the decrease of the energy release as a result of the heat consumed to melt the silicon formed in the reaction (4).

For 20% aluminum content in the system forsterite is released:

$$2MgO + SiO_2 = Mg_2SiO_4. \quad (6)$$

In this reaction forsterite is synthesized from silica and the magnesium oxide formed in the reaction (1) during com-

[3] Here and below — content by weight.

bustion of the system competes with the spinel-formation process (3).

It should be noted that the reaction (6) is made possible by the retardation of the process forming spinel because of the low content of aluminum and therefore its oxide released in the reaction (2). This is confirmed by the absence of forsterite in compositions with high aluminum content.

When aluminum is deficient in the system, the presence of a quite large amount of unreacted quartz is observed. This is explained by the hindering of the reduction of silica to silicon (4) and subsequent carbide-formation via the reaction (5).

On the whole, as the content of silica increases, the intensities of the silicon carbide, silicon, and corundum phases increase. Such behavior is explained by the reactions (4) and (5) in which silicon carbide and corundum are formed. However, when the content of aluminum in the mixture is 50% or higher the ratio of the crystalline phases changes. Thus, the silicon peaks increase and the silicon carbide peaks decrease in intensity. This is due to the reaction

$$Al + SiC = Al_4C_3 + Si. \quad (7)$$

When the aluminum content in the mixture exceeds 30%, an aluminum carbide phase is observed to precipitate, and the intensity of the diffraction peak of the phase depends on the content of magnesium carbonate in the system and increases as its content increases. This could be due to the interaction of aluminum and carbon, which is formed with reduction of carbon dioxide by aluminum (which is in excess):

$$4Al + 3CO_2 = 2Al_2O_3 + 3C; \quad (8)$$

$$4Al + 3C = Al_4C_3. \quad (9)$$

The formation and stabilization of aluminum carbide are also associated with strong reducing action of metallic aluminum. When its content is lower, oxidation of carbide by the oxygen in air as well as its interaction with silica and carbon dioxide at high temperatures are likely to occur, which thermodynamic calculations confirm. A high content of aluminum in the system (60%) results in its incomplete interaction with other components and the appearance of a solid solution of silicon in aluminum in the products of synthesis.

Figure 2 shows the dependences of the intensity of the diffraction peaks of the spinel and silicon carbide phases on the amount of aluminum with fixed carbon and magnesium carbonate content. As one can see, the curves of the intensity of the diffraction peaks of the crystalline phases and therefore their amount as function of the aluminum content are nonlinear. Such behavior can be explained by the fact that for low aluminum content (20%) the intensity of the reaction interactions is lower because of the inadequate concentration of the reducer. For a high (> 40%) content of aluminum the synthesis temperature decreases because of large thermal losses due to the high thermal conductivity of aluminum and the consumption of heat to melt aluminum, as result of which the reaction processes slow down.

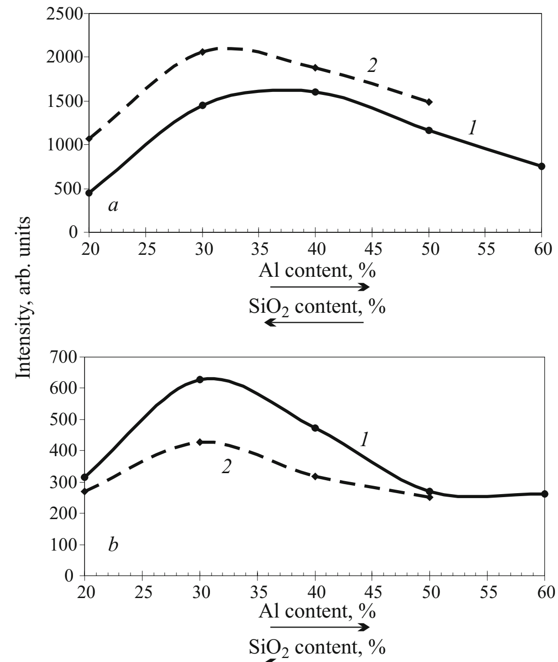

Fig. 2. Intensity of the diffraction minima of the crystalline phases of the samples versus their composition with 10% carbon content: *a*) spinel; *b*) silicon carbide; *1* and *2*) $MgCO_3$ content 20 and 30%, respectively.

As the carbon content in the system increases to 20%, the qualitative phase composition remains practically unchanged, just as the general regularities of the changes of its quantitative content. The only noticeable changes are the practically complete absence of silicon in the products of synthesis at all silica concentrations as well as a small intensification of the formation of aluminum carbide, which is due to the higher degree of completion of the carbide-forming reactions (5), (7), and (9).

Comparing the intensities of the diffraction maxima of the main phases in the products of synthesis for carbon content 10 and 20% as well as aluminum content 30% (Fig. 3) shows that an increase of the carbon concentration in the mixture results in a lower spinel yield and higher amount of silicon carbide. The decrease of the spinel yield in the synthesis process is due to the small decrease of the process temperature because of the removal heat with the gas formed with oxidation of the carbon by the oxygen in air, which is present in the pores of the sample and diffuses from the surrounding environment.

The microstructure of the samples as a function of their composition with 10% carbon content in the mixture is presented in Fig. 4. Evidently, the structure of the samples depends strongly on the content of the components. For example, for 20 and 50% aluminum content the crystal structure of the samples is indistinct. This is due to the incompleteness of the crystallization processes because of the low temperature of the process. As elemental analysis showed, the spherical inclusions consist of a solid solution of silicon in aluminum.

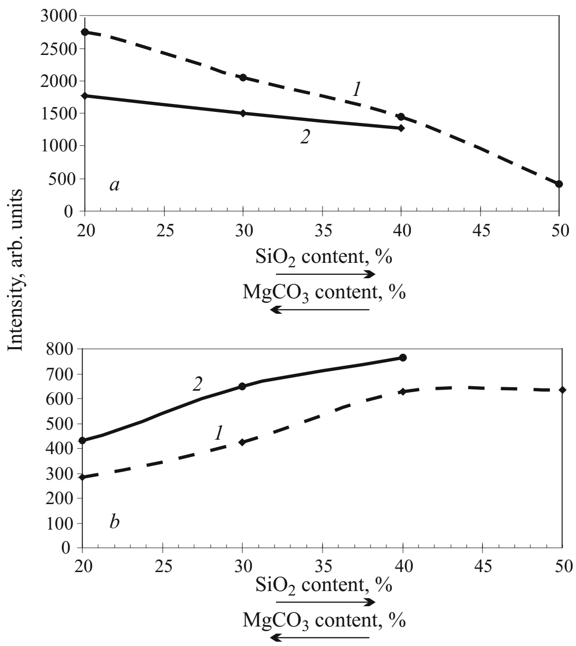

Fig. 3. Intensity of the diffraction maxima of the crystalline phase of the samples versus the composition with 30% aluminum content: *a*) spinel; *b*) silicon carbide; *1*, *2*) carbon content 10 and 20%, respectively.

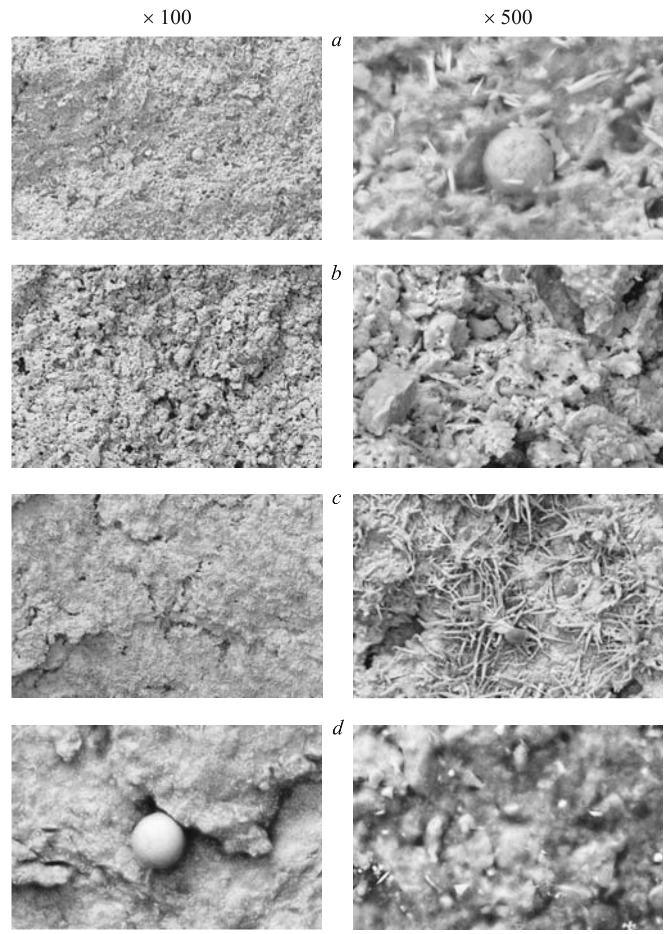

Fig. 4. Microstructure of the samples versus the content (%) of the components: *a*) 20 Al, 30 SiO_2; *b*) 30 Al, 30 SiO_2; *c*) 40 Al, 40 SiO_2; *d*) 60 Al, 20 SiO_2.

The spherical shape of the formations indicates that during synthesis the elements were in a fused state. As it cools down the melt assumes a spherical shape under the action of surface tension forces, this shape being characterized by the minimum surface area. This makes it possible to conclude that in the SHS wave aluminum melts and the silica dissolves and interacts with the aluminum. Solid particles of Al_2O_3 are formed at the SiO_2(solid) – Al(liq) interface, and the silicon dissolves in the liquid aluminum and interacts with the carbon that is partially dissolved in the aluminum, as a result of which the solid products obtained SiC and Al_4C_3 precipitate from the melt. Heterogeneous interaction at the melt – C(solid) interface with formation of SiC and Al_4C_3 grains is also possible.

The microstructure of the samples with aluminum content 30 and 40% is represented by crystals of different shape. For example, according to data from elemental analysis, whisker formations (see Fig. 4*c*) contain more than 85% Al_2O_3, i.e., corundum. It is likely that for high silica contents (in this case — 40%) the interaction of the components with formation of silicon carbide and corundum via the reaction (4) predominates. In the presence of silica, corundum crystallizes in the form of whiskers.

The crystal structure of the samples obtained from a mixture with 30 % aluminum content is represented by spinel crystals with different shapes; silicon carbide whiskers are also noticeable.

Thus, the present studies of the phase composition in the system Al – $MgCO_3$ – SiO_2 – C have established that phase formation processes can occur during self-propagating high-temperature synthesis. The dependences of the phase composition of the composite materials formed on the ratio of the initial components were determined. As the aluminum content increases from 20 to 30% the yield of spinel and silicon carbide increases and decreases for higher amounts of aluminum. Silicon does not form in compositions if carbon is not introduced. As the carbon content increases, the yield of the crystalline phases of spinel and silicon carbide decrease as a result of a decrease of the combustion temperatures of the compositions.

In summary, the region of composition range of the initial materials where a distinct crystalline structure forms and the yield of the desired spinel and silicon carbide phases is maximized has been determined.

Our investigations have shown that ceramic composite materials based on spinel and silicon carbide phases can be produced by means of self-propagating high-temperature synthesis. The spinel-containing ceramic materials which have been developed can be used to manufacture articles used in metallurgy, in machine and instrument engineering,

in the chemical industry as refractory linings for inductors and electric resistance furnaces, crucibles for melting metals, filters for melts, high-temperature electric insulators, and articles for other uses.

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